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ABSTRACT

Understanding the fundamental metallurgy of vacuum plasma spray formed materials is the key to enhancing and developing full material properties. Investigations have shown that the microstructure of plasma sprayed materials must evolve from a powder splat morphology to a recrystallized grain structure to assure high strength and ductility. A fully, or near fully, dense material that exhibits a powder splat morphology will perform as a brittle material compared to a recrystallized grain structure for the same amount of porosity. Metallurgy and material properties of nickel, iron and copper base alloys will be presented and correlated to microstructure.

INTRODUCTION

In the course of developing the Vacuum Plasma Spray process for deposition of materials that are to be considered structural materials instead of coatings, the quality requirements for the sprayed product have changed. No longer can plasma spray formed materials be optimized by coating characteristics such as density, bond strength, hardness, etc. alone. If the material or coating is to exhibit structural characteristics such as tensile strength, ductility, fatigue life, fracture toughness, etc., it must be developed to meet more stringent microstructural requirements. Simple microstructural characteristics such as porosity, oxide content, powder splat morphology and solidification structure do not address the microstructure required to develop full material properties. As with any structural material, metallurgical considerations such as grain structure, size, recrystallization, precipitates, phases, etc. must be considered. It is through the optimization of these metallurgical characteristics that plasma spray formed materials have been made with properties better than conventional cast material and in some cases equivalent to wrought material.

PROCESS AND PROCEDURES

The Plasma Spray Forming of materials described in this article refers to the deposition of thick, 6.4 mm (0.25 inch) or greater, materials using Vacuum Plasma Spray (VPS) equipment. The facility used is located at the Marshall Space Flight Center (MSFC) in Alabama and consists of a modified Electro Plasma Inc. (EPI) VPS system. The plasma guns used for this study were all versions of the basic EPI 03C series, which are direct current 120 KW plasma torches utilizing argon\hydrogen plasmas.

All specimens discussed were made in the same basic fashion. Mandrels or suitable substrates were degreased and then inserted into the MSFC VPS chamber. The chamber was evacuated and purged with argon several times prior to the plasma start. As the EPI plasma gun is engaged, the parameters are set and stabilized. The gun is used to preheat, negative transfer arc clean the substrates, and deposit powder onto the substrates. Structures usually thicker than 6.4 mm (0.25 inches) were formed/deposited and then machined into round 6.4 mm (0.25 inches) diameter tensile specimens. The specimens are tensile tested in the as-sprayed condition and thermally processed conditions (e.g. heat treated or Hot Isostatically Pressed [HIPed] and heat treated).

MATERIALS

High purity, gas atomized Inconel 718, Stainless Steel, NARloy-A and NARloy-Z powders were plasma spray formed. The chemistries for each alloy are listed by weight percent in Table 1.

Table 1. Chemical analysis of commercial Inconel 718, Stainless Steel 347, NARloy-A, and NARloy-Z alloys.

Element (wt%)	Inconel 718	Stainless Steel 347
Ni	50-55%	9-13%
Cr	17-21%	17-19%
Nb + Ta	4.75-5.5%	0.8%
Mo	2.8-3.3%	
Ti	0.65-1.15%	
Al	0.20-0.80%	
Fe	Balance	Balance
Mn	0.35% Max	2.0% Max
Si	0.35% Max	1.0% Max
C	0.08% Max	0.08% Max
	NARloy-A	NARloy-Z
Ag	3.5%	3.0%
Zr		0.5%
Cu	96.5%	Balance

RESULTS

The unetched microstructure for Plasma Spray Formed Inconel 718 is virtually featureless, see Figure 1. No oxides are visible and porosity is less than 0.64% (measured on Leco 2001 Image Analyzer).

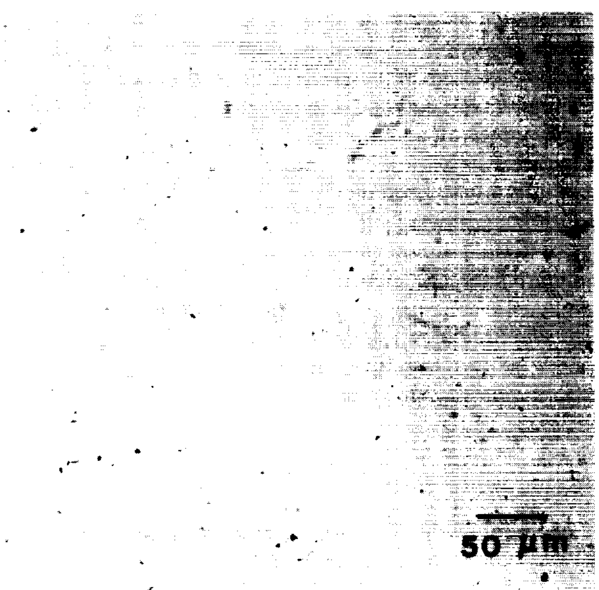


Figure 1 - Unetched microstructure of VPS Inconel 718 As-sprayed Condition (Run 90-67)

High deposition density is a requirement for good structural properties in most materials. Conventional thermal spray requirements would qualify the microstructure in Figure 1 as a good coating. However, the etched microstructure of this specimen (Figure 2) reveals a powder splat morphology where most powder particles have been thoroughly heated by the plasma and deformed into flat lamellae or splats. Occasional round powder particles (partially melted powder particles), precipitates, and pores can be seen. There is recrystallization occurring in this material, but it is all within the lamellae, and there appears to be little grain growth across lamellae boundaries. The grain size is extremely small measuring less than an ASTM 10 grain size.

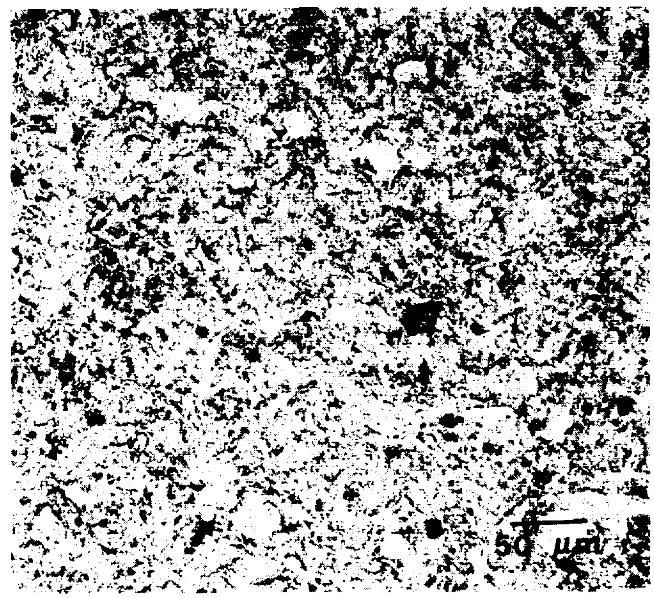


Figure 2 - Etched microstructure of VPS Inconel 718 displaying a splat type structure with minimal recrystallization and little grain growth (Run 90-67). As-sprayed condition, Kallings II etchant.

Figure 2 material's tensile strength is only that of the inter splat bonds. The tensile properties at room temperature for this material are given in Table 2.

Table 2. Room Temperature Tensile Properties of VPS Inconel 718 with a splat structure (Run 90-67) tested in the as-sprayed condition.

UTS - MPa (ksi)	876 (127)
Y.S. - MPa (ksi)	Not Detected
Elongation - %	0.2
Reduction in Area - %	0.5

The material shown in Figure 2 and Table 2 is essentially brittle with no apparent ductility or yielding. The material could be used as a coating for corrosion or wear resistance, but only for applications of compressive loading or low tensile stress. It would not be advisable to subject this material to high tensile loads since the material would tend to fail in a brittle fashion. The properties listed in Table 2 are not indicative of wrought or cast Inconel 718 or, as will be discussed later, of proper VPS Inconel 718.

Contrast the previous example of poor VPS Inconel 718 material properties with the following example. A VPS Inconel 718 totally recrystallized material with an apparent wrought like microstructure is shown in Figure 3.

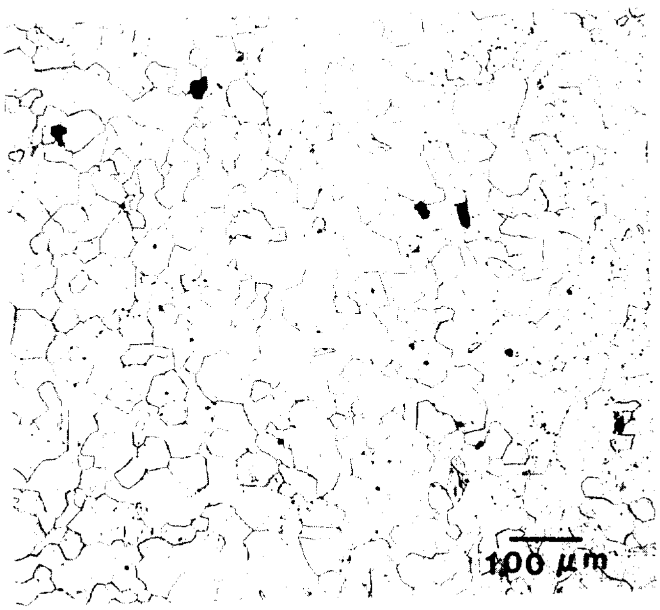


Figure 3 - Microstructure of VPS Inconel 718 recrystallized grain structure (Run 90-147). As-sprayed condition, Kallings II etchant.

The recrystallized VPS Inconel 718 material shown in Figure 3 is made from the same lot of Inconel 718 powder as the material in Figure 2, but through proper process conditions displays grain growth spanning the prior particle or splat boundaries. This material now has cohesive strength as exhibited by tensile properties listed in Table 3.

Table 3. Tensile properties of VPS Inconel 718 with a recrystallized grain structure (Run 90-147). As-sprayed condition.

	Test Temperature	
	21 C (70 F)	649 C (1200 F)
UTS - MPa (ksi)	809 (117)	775 (112)
Y.S. - MPa (ksi)	454 (65.8)	477 (69.1)
Elongation - %	47.3	36.7
Reduction in Area - %	55.0	42.6

There is a tremendous difference in the material quality of a fully recrystallized with grain growth past prior particle boundaries. The ultimate tensile strengths of materials in Tables 2 and 3 is nearly the same at room temperature, but the fully recrystallized material did yield before failing in a ductile manner. The yield strength with high ductility make this material considerable for structural applications of high tensile stress whereas the first brittle material is not. This material has properties nearly equivalent to annealed wrought or cast Inconel 718.

Table 4. Annealed * Wrought Inconel 718 tensile properties tested at room temperature. (1)

UTS - MPa (ksi)	811 (118)
Y.S. - MPa (ksi)	335 (48.5)
Elongation - %	58
Reduction in Area - %	64

* - Annealed Condition: 1066 C (1950 F) 1 hour

Fully developed plasma parameters, powder chemistry, and deposition kinetics can yield plasma spray formed materials with even better properties. High deposition temperatures combined with complete thermal processing of a HIP cycle, solution and aging heat treatment bring the VPS Inconel 718 properties to comparable levels with

solution treated and aged wrought or cast material. At room temperature, VPS Inconel 718 in both the as sprayed and the solution heat treated and aged conditions (e.g., STA) has ultimate tensile strengths exceeding cast versions of the alloy and nearly equal to forged and heat treated properties (Figure 4). The yield strength is approximately equal to cast material with ductilities exceeding wrought values. At elevated temperatures, the heat treated and HIPed and heat treated VPS Inconel 718 have yield and ultimate strengths approaching wrought material (Figure 5). The VPS material has good elevated temperature ductility which is greater than the ductility of cast material. The ductility of VPS Inconel 718 was further increased by HIPing. The solution treatment used was 1038 C (1900 F) for 30 minutes, the age cycle was 760 C (1400 F) for 10 hours and 649 C (1200 F) for 10 hours, and the HIP cycle was 1121 C (2050 F) for 4 hours at 104 MPa (15 ksi).

Figure 4:

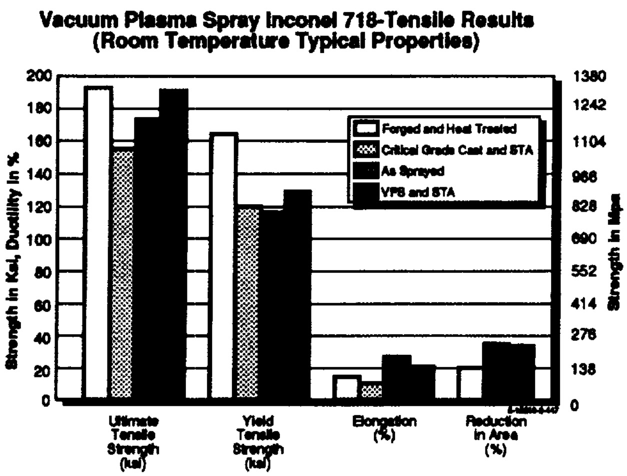
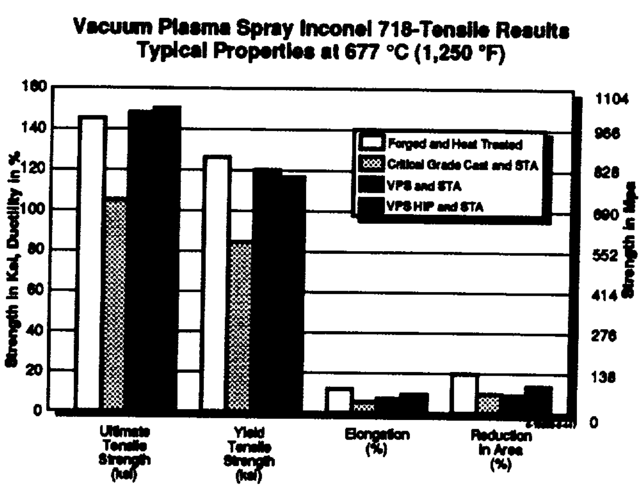


Figure 5:



The VPS Inconel 718 properties shown in Figures 4 and 5 agree with published results from other sources. (2)

The superior properties of VPS Inconel 718 shown in Table 3, and Figures 4 and 5 as compared to Table 2 are believed to be the direct result of recrystallization, grain growth and the elimination of prior particle boundaries. The recrystallization and grain growth follow conventional physical metallurgy and thermodynamic laws. Grain growth is related to processing temperature and time and can be described (for materials with small initial grain size) by:

$$D=kt^n \qquad (1)$$

where D is the mean grain diameter, t is the time at temperature, n is the grain growth exponent, and k is defined by equation (2):

$$k=k_0 e^{-Q/2RT} \qquad (2)$$

k_o is the constant of proportionality, Q is the heat of activation for grain growth, R= the international gas constant, and T= Temperature in degrees Kelvin.(3) The correlation of increased properties with increased thermal processing which drives grain growth is found in the literature for nickel and iron base alloys.(4-7) The heating time and temperature dependence can be observed in the microstructure of a material. Changes in grain size are evident in material if all the material is not given the same thermal processing. In NARloy-A a drastic difference in grain structure is displayed in Figure 6.

Figure 6 - VPS NARloy-A showing grain size changes in the as-sprayed condition resulting from differing thermal processing. Ammonium Persulfate Etchant (Run 89-171-B)

Non uniform grain structure can be caused by a rapid cool down of the material after spray deposition. The first material deposited, bottom of Figure 6, has a longer time at the high spray process temperature than the material near the surface, top of Figure 6. Hence the larger grain size of the material in the bottom of Figure 6.

For VPS formed Stainless Steel 347, the dependence on processing temperature is not as evident since the material was VPSed above 927 C (1700 F) (near the annealing temperature). The microstructures in the as sprayed and as HIPed conditions are shown in Figure 7.

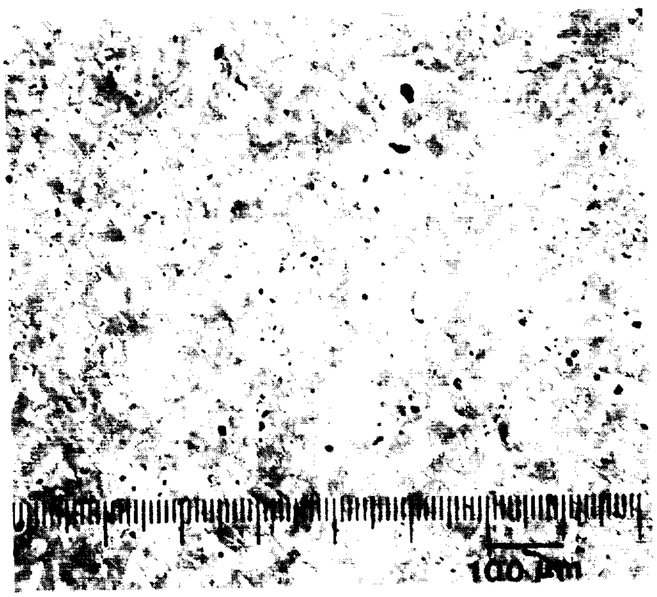


Figure 7A

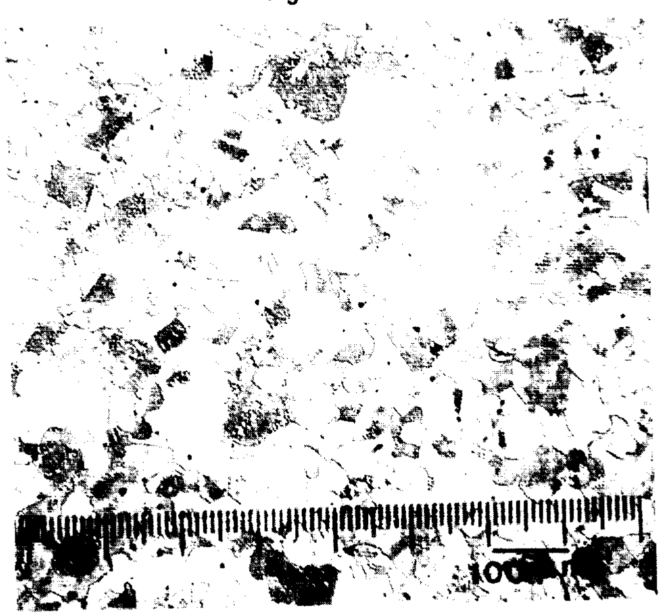


Figure 7B

Figure 7 - Vacuum Plasma Sprayed Stainless Steel 347 (Run 90-82) A. as-sprayed, B. as HIPed (1121 C [2050 F], 4 hours, 103 MPa [15 ksi]), Kallings II Etchant

The VPS Stainless Steel 347 shows a totally recrystallized structure. No evidence of powder particles or splat boundaries remains. As with the VPS Inconel 718 shown in Figure 3, this material has properties comparable to annealed wrought product (Tables 5 and 6).The grain growth and closure of porosity during HIP did increase the materials strength and ductility as evident in Tables 5 and 6.

Table 5. Vacuum Plasma Sprayed Formed Stainless Steel 347 tensile properties tested at room temperature and compared to annealed wrought product.

	VPS as-sprayed	VPS HIP*	Wrought**
UTS - MPa (ksi)	597 (86.5)	620 (89.9)	575 (83.3)
Y.S. - MPa (ksi)	252 (36.5)	297 (43.0)	230 (33.3)
Elongation - %	49.5	49.7	50.7
Reduction in Area - %	59.1	64.0	66.7

*HIP = 1121 C (2050F), 4 hours, 104 MPa (15 ksi)
**Wrought in Annealed condition (1121 C [2050 F], 30 minutes) (8)

Table 6.Vacuum Plasma Sprayed Formed Stainless Steel 347 tensile properties tested at elevated temperature (950 C [1250 F]) and compared to annealed wrought product.

	VPS HIP*	Wrought**
UTS - MPa (ksi)	406 (58.8)	284 (41.1)
Y.S. - MPa (ksi)	-----	146 (21.1)
Elongation - %	94.7	32.0
Reduction in Area - %	66.7	56.0

*HIP = 1121 C (2050F), 4 hours, 104 MPa (15 ksi)
**Wrought in Annealed condition (1121 C [2050 F], 30 minutes) (8)

The spray formed stainless steel 347 alloy compares quite favorably with the annealed wrought product both at room temperature and at elevated temperature (e.g. 677 C [1250 F]). (In Table 6, no VPS SS 347 was tested in the as sprayed condition at 677 C, and no yield strength at 677 C for the HIPed material was indicated due to equipment problems during the tests.)

DISCUSSION

More stringent microstructural requirements must be considered if plasma sprayed materials are to be employed in structural applications. A dense material with the plasma spray splat morphology in the first example may make an acceptable coating, but it could only be used for compressively loaded structures. The poor ductility arises from the fact that the material has no apparent cohesive strength or yield before fracture capability.

Strong cohesive strength can be generated for the same alloy and even same powder through optimization of the plasma parameters, powder parameters, deposition kinetics, and understanding of the metallurgy. The Inconel 718 material in the second example (Figure 3), and the Stainless Steel 347 in the final example with recrystallized grains and grain growth spanning the prior particle or splat boundaries have properties equivalent to annealed wrought or cast product. In third example (Figures 4 and 5) the fully heat treated Plasma Spray Formed Inconel 718 compared favorably to the fully heat treated wrought and cast product.

The factors influencing optimization of the plasma parameters must include: arc and secondary gases and mass flow rate, arc power, plasma velocity, and enthalpy. The factors influencing the powder parameters must include: chemistry, oxygen content, powder size, and powder injection parameters. For deposition kinetics, the process must be developed considering the impact state of splats/particles, part temperature, particle temperature, time of spray, (and others). With all these important plasma parameters, the resulting metallurgy of the material must be considered.

For deposition of a complex precipitation strengthened alloy such as Inconel 718, the Time, Temperature, Transformation Diagram, Figure 8 (9), must be consulted to determine optimum deposition temperature with respect to phase precipitation. VPS Inconel 718 deposited at 871 - 927 C (1600-1700 F), the first example, will precipitate brittle delta (∂) phase. VPS Inconel 718 deposited above 1038 C (1900 F), example 2, and cooled quickly will not precipitate brittle undesirable phases and will exhibit characteristic annealed properties. Inconel 718 material fully heat treated to precipitate gamma and gamma prime phases will be strengthened as are wrought and cast Inconel 718 product. Other factors like the temperature and time required for recrystallization (which for Inconel 718 does not start until 857 C [1575 F] for heavily cold worked material) (10) must be considered, and the deposition temperature adjusted to exceed the recrystallization temperature. Otherwise brittle material may form during deposition.

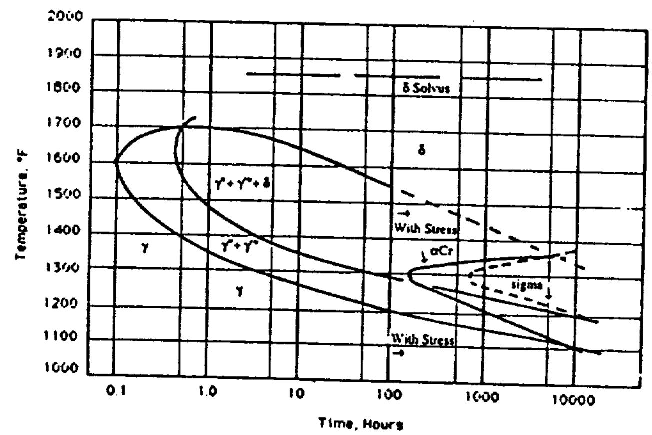


Figure 8 - Time Temperature Transformation Curve (T-T-T Diagram) for Inconel 718. (9)

Many studies can be conducted to address the effects of plasma parameters on structural properties, but the characterization criteria must be established based on structural material methods. For structural applications, plasma spray formed materials must have material properties that meet the application requirements. To do this, these spray formed materials must incorporate acceptable microstructures. Due to the fine equiaxed grain size developed by originating from fine powder, the VPS material will always have slightly different properties than cast or wrought product. In some applications, the fine grain size and unique properties of VPS materials can be used to tailor make each material for a specific application.

SUMMARY

The Vacuum Plasma Spray process can be used to spray form material with the properties of structural alloys. Studies for Inconel 718, Stainless Steel 347, NARloy-A, and Narloy-Z (11) have shown spray formed materials can have material properties of the wrought or cast form. However plasma spray formed materials with only a powder splat type, unrecrystallized microstructure will have poor properties compared to spray materials with recrystallized and larger grain size microstructures. Important processing parameters need to include not only the plasma spray parameters, but the deposition time and temperature requirements which govern recrystallization, grain growth, and phase transformation.

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